[Translation from Japanese]

(19) Japanese Patent Office (JP)

(12) Official Gazette of Unexamined Patent Applications (A)

(11) Patent Application Publication No: **55-36266**

(43) Patent Application Publication Date: March 13, 1980

---

(51) Int. Cl.^{3}		Identification Code	Internal File Nos.
C 08 L	9/00		6613-4J
B 29 H	17/00		7166-4F
B 60 C	1/00		6948-3D
	5/12		6948-3D
C 08 K	5/32		

Number of Inventions: 1
Request for Examination: Not yet received (Total of 5 Pages)

---

(54) Title of the Invention: **Tubeless Tire**

(21) Patent Application No: 53-110276

(22) Patent Application Date: September 7, 1978

(72) Inventor: Yoshiki MAYAMA
3-9, Tendomachi, Nishimiya

(72) Inventor: Akira ARASE
6-144, Morimoto, Itami

(71) Applicant: Toyo Tire & Rubber Co., Ltd.
1-17-18, Edobori, Nishi-ku, Osaka

(74) Agent: Takeo OSHIMA, Patent Attorney (and 1 other)

Specification

1. Title of the Invention

Tubeless Tire

2. Claims

(1) A tubeless tire, wherein a rubber layer for preventing air permeation containing 40 to 100 ppw of halogenated butyl rubber, 60 to 0 ppw of one or two or more rubbers selected from a group of natural rubbers and diene-based synthetic rubbers, and additives such as a vulcanizer, an accelerator and carbon black, and an intermediate reinforcing rubber layer containing 100 ppw of one or two or more rubbers selected from a group of natural rubbers and diene-based synthetic rubbers, 0.05 to 1 ppw of N-(2-methyl-2-nitropropyl)-4-nitrosoaniline, and common additives such as a vulcanizer, an accelerator and carbon black are formed separately, wherein the rubber sheets of both layers are integrated using the application of force, wherein the integrated rubber sheet is applied on the inside surface of the tire against the first carcass ply with the reinforced intermediate layer on the inside, and wherein the tire is molded and vulcanized.

(2) The tubeless tire described in claim 1, wherein the 300% modulus value is 4 kg/cm^2 or greater when the intermediate reinforcing rubber layer is unvulcanized.

3. Detailed Description of the Invention

The present invention relates to a tubeless tire and is noteworthy for reducing the weight of a tire while retaining the durability and air retention characteristics of a tubeless tire for a passenger vehicle.

In order to maintain air retention properties, a tubeless tire of the prior art has a rubber sheet serving as an air permeation preventing layer bonded to the inside of the tire. This rubber sheet consists of a single rubber component or a mixture of two or more rubber components such as natural rubber or a diene-based synthetic rubber and some common additives. (This rubber sheet is often referred to as an inner liner.) Unfortunately, diene-based polymers are highly permeable to air and so the sheet has to be thick in order to serve as an air permeation preventing layer. This prevents permeable dispersion inside a tire body filled with air under pressure.

However, in order to improve the safety and reliability of tires, there have been calls for a reduction in the amount of heat generated during travel. There have also been calls for reducing the weight of tires in order to lower material consumption.

Several tire makers both at home and abroad have experimented with forming a thin air permeation preventing layer using halogenated butyl rubbers which have low air permeability.

Unfortunately, when the crown of a green tire molded into a cylindrical shape is expanded to create a toroidal shape and the tire is vulcanized, the unvulcanized layer containing the halogenated butyl rubber slips off the nylon or

polyester cords. Because the Green Modulus is low at this time, the tire is easily roll pressed and the cords are initially compressed inside the vulcanizer. Subsidence occurs among adjacent tire cords causing unevenness. The vulcanized rubber layer on the cords becomes thinner, and traveling and the internal tire pressure cause the further subsidence inside the cords. As a result, air penetrates into the cords, and separation and cracking occur. For this reason, it has been difficult to make the air permeation preventing layer thinner.

However, the present inventors have discovered a means of making a thinner layer while maintaining air retention properties and durability or the prior art. This has allowed them to create a lighter weight tire.

In the resultant invention, the inner liner has a two-layer composition consisting of different elastomers. These layers are integrated into a single sheet through the application of force. One layer provides air permeation prevention, and the other layer provides reinforcement. The modulus of the unvulcanized rubber, or the Green Modulus (GM), in the reinforcing layer is high. This helps solve the problem associated with the prior art. This layer is bonded to the carcass ply of the tire to form an intermediate reinforcing layer. This also helps solve the problem associated with the prior art.

The air permeability of the vulcanized rubber depends on the ratio of chlorinated butyl rubber to natural rubber and tends to follow the curve shown in FIG 1. This is known to be true of all blended elastomers containing diene-based rubbers in addition to natural rubber.

In this graph, the lower curve indicates the air permeability at 35°C and the upper curve indicates the air permeability at 65°C.

Therefore, the elastomer used in the air permeation preventing layer has to contain at least 40 ppw of halogenated butyl rubber.

In other words, the rubber layer for preventing air permeation contains 40 to 100 ppw of halogenated butyl rubber and 60 to 0 ppw of one or two or more rubbers selected from a group of natural rubbers and diene-based synthetic rubbers. To 100 ppw of this rubber mixture is included additives such as a vulcanizer, an accelerator and carbon black. This rubber composition is then formed into a sheet.

In order to provide the intermediate reinforcing layer with the required high Green Modulus, different types and amounts of carbon black can be added to the rubber composition. N-(2-methyl-2-nitropropyl)-4-nitrosoaniline is also known to achieve this effect. Unfortunately, as shown in the basic compositions in Table 1, the former, carbon black, increases the amount of heat generated in addition to increasing the Green Modulus (GM). Therefore, the Green Modulus has to be raised as high as possible while avoiding use of more than 50 ppw carbon black.

Basic Components	ppw
SBR 1500	20
RSS #3	60
ZnO	3
Stearic Acid	2
Anti-Aging Agent	2
Processing Oil	10
Vulcanization Accelerator (Noxera-MSA)	1
Sulfur	2.5
Carbon Black	Variable

Table 1

Carbon Black (ppw)		Mooney Viscosity (MLi + 4)	Green Modulus (100% GM)	Heat Generation ($\Delta T°C$)
HAF	50	42	1.4	17
	60	50	1.8	19
	70	55	1.9	20
	80	-	-	-
FEF	50	38	1.3	13
	60	44	1.7	17
	70	49	1.9	18
	80	60	2.2	20
GPF	50	36	1.2	10
	60	38	1.4	13
	70	42	1.6	14
	80	46	2.0	16

The latter has the advantage of increasing the Green Modulus while holding down the amount of heat generated. The relationship between the amount added and the Greens Modulus (GM) is shown in FIG 2. The curves for the three compositions shown in Table 2 are indicated.

Table 2 **ppw**

Component / Composition No.	I	II	III
RSS #3	85	50	-
SBR 1500	15	-	-
Halogenated Butyl Rubber	-	50	100
Zinc Oxide No. 3	3	3	3
Stearic Acid	2.5	2.5	2.5
Anti-Aging Agent	2	-	-
Carbon Black	50	50	50
Processing Oil	10	10	10
Accelerator (Noxera-MSA)	1.2	1.2	1.2
Sulfur	2	-	-
Alkyl Phenol Disulfide	-	1	1
N-(2-Methyl-2-Nitropropyl)-4-Nitrosoanliline	0~1.0	0~1.0	0~1.0

As seen in the results for Composition No. III, N-(2-Methyl-2-Nitropropyl)-4-Nitrosoanliline had little effect on the halogenated butyl rubber, but a small amount increased the Green Modulus of rubber compositions containing natural rubber and diene-based synthetic rubbers.

The elastomer composition for the intermediate reinforcing layer contains 0.005 to 1 ppw of N-(2-methyl-2-nitropropyl)-4-nitrosoanliline. The present inventors discovered in their research that an amount in this range was sufficient to raise the Green Modulus or 300% modulus of the unvulcanized rubber composition above 4 kg/cm^2.

In other words, the intermediate reinforcing rubber layer contains 100 ppw of one or two or more rubbers selected from a group of natural rubbers and diene-based synthetic rubbers, 0.05 to 1 ppw of N-(2-methyl-2-nitropropyl)-4-nitrosoaniline, and common additives such as a vulcanizer, an accelerator and carbon black. This rubber composition is formed into a sheet. Force is then applied to the air permeation preventing rubber sheet and the intermediate reinforcing rubber sheet to form a single sheet or inner liner.

In order to form the single sheet or inner liner with satisfactory adherence, the two rubber sheets should be simultaneously roll pressed. The intermediate reinforcing layer side of the inner liner is adhered to the first carcass ply inside the tire, and the resultant configuration molded and vulcanized to obtain a tubeless tire.

The thickness of the air permeation preventing layer should be within the 0.3 mm to 1 mm range. If too thin, the air permeation is too high. If too thick, the tire becomes too heavy.

The thickness of the reinforcing intermediate layer should be within the 0.5 mm to 1 mm range. If too thin, it does not prevent subsidence of the air permeation preventing layer into the cords. If too thick, it increases the weight of the tire and the amount of heat generated by the tire. The total thickness of both layers should be no greater than 2.3 mm.

During the manufacture of tires, the Green Modulus of the inner liner layer is increased and the resultant bias and fluidity improves the localized imbalance in the carcass ply cords. This also has the effect of preventing localized reductions in the thickness of the rubber coating on the ply cords. The manufacture of tires with uniform layers thus becomes possible.

The following is a detailed explanation of the present invention with reference to working examples.

The various component compositions in the working examples are shown in Table 3. These were combined in the working examples with the different dimensions shown in Table 4 and Table 5. A rubber sheet consisting of air permeation preventing layer rubber and intermediate reinforcing layer rubber were simultaneously roll pressed to form the inner liner. The inner liner was then bonded to the first carcass ply on the inside surface of the tire with the intermediate reinforcing layer on the inside. The resultant molded and

vulcanized 165SR13 tubeless tires were then tested and compared. The results are shown in the tables.

The various component compositions are shown in Table 3.

Compositions C, D and E are for the intermediate reinforcing layer used in the tubeless tires of the present invention. Here, A, B and F denote other compositions. Compositions K, L and M are for the air permeation preventing layer used in the tubeless tires of the present invention.

Table 4 and Table 5 show the testing results.

Table 3

Component / Compositions	A	B	C	D	E	F	K	L	M
IR	-	-	-	-	85	-	-	-	-
RSS #3	50	85	85	100	-	85	50	30	-
SBR 1500	50	15	15	-	15	15	-	-	-
Chlorinated IIR	-	-	-	-	-	-	50	-	100
Sulfurized IIR	-	-	-	-	-	-	-	70	-
Carbon Black	50	45	45	50	50	60	50	50	50
Processing Oil	10	7	7	10	10	7	10	10	10
Zinc Oxide No. 3	3	3	3	3	3	3	5	5	5
Stearic Acid	2.5	2.5	2.5	2.5	2.5	2.5	3.5	3.5	3.5
Anti-Aging Agent	1.5	2.0	2.0	1.5	1.5	2	-	-	-
N-(2-Methyl-2-Nitropropyl)-4-Nitrosoanliline	-	-	0.2	0.05	0.8	-	-	-	-
Accelerator (Noxera-MSA)	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2
Sulfur	2.0	2.0	2.0	2.0	2.0	2.0	-	-	-
Alkyl Phenol Disulfide	-	-	-	-	-	-	1.0	1.0	1.0
Non-Vulcanized 300% Modulus (kg/cm^2)	1.7	2.5	5.2	4.2	4.7	4.1	-	-	-

(Notes) IR Synthetic Isoprene Rubber

RSS #3 Natural Rubber, Smoke Sheet No. 3

SBR 1500 Styrene-Butadiene

IIR Butyl Rubber

Table 4

Component/ Sample No.	Prior Art	Present Invention				
	0	1	2	3	4	5
Inner Liner Thickness Pre (mm)	2.5	2.0	1.7	1.5	1.8	1.3
Component No.	A	C + K	C + K	D + M	E + L	C + E
Layer Thickness (mm)	2.5	1.0 + 1.0	1.0 + 0.7	1.0 + 0.5	0.9 + 0.9	0.6 + 0.7
Inner Liner Thickness Post (mm)	1.55	1.25	0.97	0.95	1.10	0.75
Tire Weight (kg)	7.70	7.45	7.35	7.25	7.40	7.20
Air Pressure Retention (kg/cm^2)*	1.40	1.45	1.40	1.60	1.45	1.40
Drum Test (Km)**	18,000	19,000	18,000	20,000	20,000	18,000

(Notes) * Initial Air Pressure 2.0 kg/cm^2, Air Pressure After 20 Days in 80°C Oven

** General Durability Test, 160% JIS Standard Load at 80 Km/hr

Table 5

Component/ Sample No.	Comparative Examples					
	6	7	8	9	10	11
Inner Liner Thickness Pre (mm)	1.1	2.0	2.0	1.7	1.7	1.7
Component No.	C + K	B + K	F + K	K	L	M
Layer Thickness (mm)	0.4+0.7	1.0+1.0	1.0+1.0	1.7	1.7	1.7
Inner Liner Thickness Post (mm)	0.68	0.95	1.26	0.96	0.90	0.9
Tire Weight (kg)	7.15	7.45	7.5	7.35	7.35	7.35
Air Pressure Retention (kg/cm^2)	1.40	1.35	1.35	1.40	1.45	1.55
Drum Test (Km)	15,000	16,000	16,000	12,000	12,000	9,000

In the working examples, a rubber layer for preventing air permeation is formed from 40 to 100 ppw of halogenated butyl rubber and 60 to 0 ppw of diene-based synthetic rubbers, the intermediate reinforcing rubber layer is formed from 100 ppw of diene-based synthetic rubber and 0.05 to 1 ppw of N-(2-methyl-2-nitropropyl)-4-nitrosoaniline, the rubber sheets of both layers are

simultaneously roll pressed to form an integrated sheet or inner liner that achieves the purpose of the present invention. In other words, the inner liner of the present invention is thinner than an inner liner of the prior art, but is able to maintain favorable air retention and durability.

4. Brief Explanation of the Drawings

FIG 1 is a graph showing the air permeability curve with respect to the amount of chlorinated butyl rubber in the elastomer. In this graph, the x-axis indicates the ratio of chlorinated butyl rubber (Cl-IIN) to natural rubber (NR) in the composition, and the y-axis indicates the degree of air permeability.

FIG 2 is a graph showing the Green Modulus (GM) curve for various rubber compositions (Composition Nos. I, II and III) with respect to the amount of N-(2-methyl-2-nitropropyl)-4-nitrosoaniline added. In this graph, the x-axis indicates the amount added and the y-axis indicates the 300% Green Modulus.

Agent Takeo OSHIMA, Patent Attorney

[Keys to text in figures:]

FIG 1

[y-axis] Air Permeability Q x 10^{-8}

FIG 2

[x-axis] Amount Added (PHR)

[y-axis] Green Modulus (300% gm/mm^2)